Ag ALLOY FILM FOR ELECTRONIC PARTS, AND SPUTTERING TARGET FOR DEPOSITING Ag ALLOY FILM

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Inventor(s): MURATA HIDEO; TAKAHASHI TSUTOMU; ONODERA IKUO
Applicant(s): HITACHI METALS LTD; GEOMATEC CO LTD
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Abstract of **JP 2003089830 (A)**
PROBLEM TO BE SOLVED: To provide an Ag alloy film for electronic parts which jointly has high reflectivity, low resistance, and heat resistance and corrosion resistance in a process, and has improved adhesion to a substrate as well, and to provide a sputtering target for depositing the Ag alloy film. SOLUTION: The Ag alloy film for electronic parts has a composition containing one or more kinds of elements selected from the group consisting of Ce, Nd and Gd, by 0.1 to 2 at.% in total, and one or more kinds of elements selected from the group consisting of Cu, Au, Pd and Pt by 0.1 to 1 at.% in total, and the balance substantially Ag. Alternatively, the Ag alloy for electronic parts contains 0.1 to 0.45 at.% Pd selected from the group consisting of Cu, Au, Pd and Pt. The sputtering target for depositing an Ag alloy film has the componential composition same as those of the above films.

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[Claim(s)]
[Claim 1]An Ag alloy film for electronic parts becoming a 0.1-1at% implication and a remainder real target from Ag in total 0.1 - 2at% about one sort or two sorts or more of elements further chosen from a group of Cu, Au, Pd, and Pt in one sort or two sorts or more of elements chosen from a group of Ce, Nd, and Gd.
[Claim 2]choosing Pd from a group of Cu, Au, Pd, and Pt -- Pd -- 0.1 - 0.45at% -- the containing Ag alloy film for electronic parts according to claim 1.
[Claim 3]In total one sort or two sorts or more of elements chosen from a group of Ce, Nd, and Gd 0.1 - 2at%, A sputtering target for Ag alloy film formation becoming a 0.1-1at% implication and a remainder real target from Ag in total about one sort or two sorts or more of elements furthermore chosen from a group of Cu, Au, Pd, and Pt.
[Claim 4]choosing Pd from a group of Cu, Au, Pd, and Pt -- Pd -- 0.1 - 0.45at% -- the containing sputtering target for Ag alloy film formation according to claim 3.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention, for example A liquid crystal display, a plasma display panel. In plane display devices, such as (the following, PDP), a field emission display (following, FED), and electroluminescence (following, EL), and the electrophoresis type display used for electronic paper etc., It is related with the Ag alloy film for electronic parts and the sputtering target for Ag alloy film formation in which a high optical reflectance, and corrosion resistance, patterning nature, ductility and adhesion are demanded.

[0002]
[Description of the Prior Art]Conventionally, the transmissive liquid crystal display of the liquid crystal display

which has high display quality by building in a light source (lamp) and glaring from the back was common. However, there was a problem said that the power consumption of transmissive liquid crystal display of the backlight which is a light source is large, and a hour of use becomes short as a Personal Digital Assistant of a cell drive. For this reason, development of the reflective liquid crystal display which uses outdoor daylight efficiently and does not use backlight fundamentally, and development of the transflective type liquid crystal display which combined the reflected type and the conventional penetrated type are performed in recent years.

[0003]Many aluminum or the aluminum alloy thin films of the reflectance of a visible light range which are an element whose electric resistance it is high and is also low have been used for the electrode which is the reflection film, reflection film, and electric conduction film which are used for such a reflected type and a transflective type display, and the display use which makes a wiring film serve a double purpose also in metal. However, the reflection film is asked for flat reflective characteristics in recent years by the high reflection and visible light range which are called a paper white for the display improved quality of a display. In order to attain highly minute-ization, a low resistance material is called for. For this reason, Ag [higher a reflectance than aluminum and low resistance] attracts attention.

[0004]

[Problem to be solved by the invention]In the case of above-mentioned aluminum system reflection film, a hillock etc. occur in the heating process in the manufacturing process of a liquid crystal display, and there is a problem to which a reflectance falls with grain growth. For this reason, the aluminum alloy which adds January the 15th of the lunar calendar matter for corrosion resistance which is transition metals, such as Ti and Ta, is used for aluminum for inhibition of the above-mentioned hillock or grain growth. The reflectance reduction at the time of liquid crystal display manufacture can be controlled with this aluminum alloy. However, there is a problem to which the reflectance of a material itself falls.

[0005]On the other hand, in the case of Ag reflection film whose reflectance is higher than aluminum, there is a problem that the adhesion over glass and plastics which are the substrates for liquid crystal displays is low, and peeling arises in a process. It originates in this adhesion being low, and a film condenses by the heating process at the time of manufacture of a display, etc., and a reflectance falls sharply, and resistance will increase. Corrosion resistance is low, and after forming membranes on a substrate, it discolors only by neglecting [about] it to the air on the 1st, and becomes reflective characteristics which are tinged with the yellow taste. And it was corroded by the drug solution used at the time of manufacture of a display, the reflectance fell sharply, and there was a problem which resistance also increases.

[0006]in order to solve the above problem -- JP,9-324264,A -- Au -- 0.1 - 2.5at% and Cu -- 0.3 - 3at% -- the Ag alloy in which the added Ag alloy added Pt, Pd, Au, Cu, and nickel on the glue line to JP,11-119664,A is proposed. Although uses differ, as a reflection film -- JP,2000-109943,A -- Ag -- Pd -- 0.5 - 4.5at% -- the added alloy -- JP,2001-192752,A -- Ag -- Pd -- 0.1 - 3wt%, aluminum, Au, Pt, Cu, Ta, Cr, Ti, etc. -- 0.1 - 3wt% -- the contained alloy is proposed.

[0007]However, a reflectance falls only by adding slightly and Pd, nickel, etc. have especially the problem that decline in the reflectance by the side of the low wavelength of a visible light range is large. When Au and Cu are added, there is little decline in a reflectance, but there is a problem in a heat-resisting property. If Ta, Cr, and Ti are added, while a reflectance will fall, resistance will increase sharply, and the low resistance feature which Ag has will be lost.

[0008]Plane display devices [purpose / of this invention] for example, such as reflective liquid crystal display, FED, and organic electroluminescence, The high reflectance and low resistance which are demanded in a curved surface display device with a flexible resin film board etc., etc., It has a heat-resisting property in the inside of a process, and corrosion resistance, and is in providing the sputtering target for forming the Ag alloy film for electronic parts which has improved the adhesion to a substrate further, and its Ag alloy film.

[0009]

[Means for solving problem][by considering it as the reflection film which added the element chosen as Ag as a result of inquiring wholeheartedly so that this invention persons may solve above-mentioned SUBJECT] The heat-resisting property and the resistance to environment were improved without reducing greatly the high reflectance which Ag originally has, it found out that the adhesion to a substrate was also further improvable, and this invention was reached.

[0010]This invention in total one sort or two sorts or more of elements chosen from the group of Ce, Nd, and Gd Namely, 0.1 - 2at%, It is an Ag alloy film for electronic parts becoming a 0.1-1at% implication and a remainder real target from Ag in total about one sort or two sorts or more of elements furthermore chosen from the group of Cu, Au, Pd, and Pt. choosing Pd from the group of Cu, Au, Pd, and Pt before long -- Pd -- 0.1 - 0.45at% -- it is a containing Ag alloy film for electronic parts.

[0011]This invention in total one sort or two sorts or more of elements chosen from the group of Ce, Nd, and Gd 0.1 - 2at%, It is a sputtering target for Ag alloy film formation becoming a 0.1-1at% implication and a remainder real target from Ag in total about one sort or two sorts or more of elements furthermore chosen from the group of Cu, Au, Pd, and Pt. choosing Pd from the group of Cu, Au, Pd, and Pt before long -- Pd -- 0.1 - 0.45at% -- it is a containing sputtering target for Ag alloy film formation.

[0012]

[Mode for carrying out the invention]The feature of this invention is in the place which found out the optimal alloy composition for compensating SUBJECT called the adhesion, the corrosion resistance, and the heat-resisting property which the Ag film has based on Ag with a high reflectance of the material itself. In total one sort or two sorts or more of elements chosen from the group of Ce, Nd, and Gd specifically 0.1 - 2at%, In total, are one sort or two sorts or more of elements furthermore chosen from the group of Cu, Au, Pd, and Pt an Ag alloy film for electronic parts which becomes a 0.1-1at% implication and a remainder real target from Ag, and especially, choosing Pd from the group of the Cu, Au, Pd, and Pt -- Pd -- 0.1 - 0.45at% -- it is an included Ag alloy film for electronic parts. And if it is a sputtering target of the presentation, it is effective in formation of the Ag alloy film of this invention.

[0013]Usually, although the reflectance as a film is high when the reflection film of Ag is produced, it is as above-mentioned that there is a problem that a reflectance will fall in the process at the time of producing products (for example, liquid crystal display etc.) using the reflection film. [then by adding one sort or two sorts or more of elements / a proper quantity of / chosen from the group of one sort or two sorts or more of elements chosen as Ag from the group of Ce, Nd, and Gd, Cu, Au, Pd, and Pt in this invention] The reflection film which controlled decline in the reflectance in a process process can be produced without reducing the reflectance of the material itself greatly.

[0014]For example, in the manufacturing process of products, such as a liquid crystal display and organic electroluminescence, after forming the reflection film, the process accompanied by a number of times heat-

treatment is, and as for Ag reflection film, a reflectance falls according to the heating process in that case. That is, film growth, condensation, etc. by heating take place, a membrane surface serves as more irregular shape, or a void generates it. And a membrane surface discolors depending on the heating atmosphere, and this also causes decline in a reflectance. In this case, even if it is, the Ag alloy film for electronic parts of this invention can maintain a high reflectance. And since there is also little deterioration of the film itself, low resistance is also maintainable.

[0015]one sort or two sorts or more of elements in which the Ag alloy film of this invention is chosen from the group of Ce, Nd, and Gd -- the sum total -- 0.1 - 2at%, one sort further chosen from the group of Cu, Au, Pd, and Pt, or two sorts or more of elements -- the sum total -- 0.1 - 1at% -- it adds. This is because sufficient reflectance cannot be maintained and secured less than [0.1at%] if there is no corrosion-resistant improvement effect according [the total quantity of Ce, Nd, and Gd] to the content and 2at% is exceeded. It is 0.2 - 0.5at% preferably, and, in addition to a still higher reflectance, is desirable also in also after a heat-resisting property improves.

[0016]The total quantity of one sort or two sorts or more of elements chosen from the group of Cu, Au, Pd, and Pt which are added simultaneously has few depression effects of a hillock less than [0.1at%], and if 1at% is exceeded, the reflectance by the side of the low wavelength of a visible light range will fall. Therefore, Cu, Au, Pd, and Pt may be 0.1 - 1at% in total. Pd is preferred for maintaining membranous low resistance among these elements. When Pd is chosen, it becomes possible to obtain a still higher reflectance and the low resistance Ag alloy film for electronic parts by making Pd into 0.1 - 0.45at%.

[0017]Maintenance of the reflection film by content of the above-mentioned element group of this invention of the reflectance or the Reason for improvement is not clear. However, it is thought that the alloying element of Ce, Nd, and Gd which were selected by this invention tends to form Ag and a compound, it controls Ag intergranular corrosion since it deposits easily to a grain boundary, and it raises a resistance to environment. And a melting point is still higher than Ag, by adding Cu, Au, Pd, and Pt which are easily mixed with Ag, atomic diffusion is delayed, the development of a hillock is controlled, and it is thought that a high reflectance is maintainable.

[0018]Since the grain growth and the condensation accompanying movement of the atom in a heating process are controlled by a deposit of the compound of Ag and Ce in a grain boundary, Nd, and Gd, and the mutual effect of Cu, Au, Pd, and Pt of stagnating in a grain, a heat-resisting property improves. And since it becomes a film form of the detailed and smooth surface, decline in a reflectance can be controlled. To improve adhesion is considered by the effect that membrane stress is reduced by addition of these elements, and the effect of both condensation inhibition.

[0019]As for an Ag alloy film for electronic parts of this invention, in order to obtain a stable reflectance, it is preferred to be referred to as 50-300 nm as thickness. Membranous surface type voice changes easily that it is less than 50 nm, and when it uses for a plane display device further, in order that light may penetrate, a reflectance falls. On the other hand, although a reflectance does not change a lot that it is the thickness over 300 nm, when forming a film, it takes time. When using as a diffusion shell, it is possible to be referred to as 10-50 nm.

[0020]When forming an Ag alloy film for electronic parts of this invention, sputtering using a target is the optimal. It is because a film of the presentation can form easily mostly with a target material by the sputtering method, and it becomes possible to form stably an Ag alloy film for electronic parts of this

invention. [for this reason a sputtering target of this invention] It becomes a 0.1-1at% implication and a remainder real target from Ag in total 0.1 - 2at% about one sort or two sorts or more of elements further chosen from a group of Cu, Au, Pd, and Pt in one sort or two sorts or more of elements chosen from a group of Ce, Nd, and Gd. and a case where Pd is chosen from a group of Cu, Au, Pd, and Pt -- Pd -- 0.1 - 0.45at% -- it is an included sputtering target.

[0021]What is necessary is just to be able to attain a high grade, a uniform organization, high density, etc. which are generally required of a target, although it is variously about the manufacturing method of a target. For example, after adjusting to a predetermined presentation with a vacuum melting process, it casts to metal molds, tabular is further processed by forging, rolling, etc. after that, and it can manufacture by making the target of predetermined shape by machining.

[0022]A thin film can be formed by sputtering and what is necessary is it to be preferred to use a glass substrate and a Si wafer as a substrate used in that case, when forming the Ag alloy film for electronic parts of this invention by sputtering, but just to be a resin substrate and a metal substrate.

[0023]

[Working example](Embodiment 1) After having adjusted, having cast in the vacuum melting process, having produced the ingot so that it might become substantially the same as that of the target system of the Ag alloy film for electronic parts to evaluate, and processing tabular by cold rolling, the target (100 mm in diameter and 5 mm in thickness) was produced by machining. The pure Ag film which formed the Ag alloy film of 200 nm of thickness on the glass substrate with the smooth surface or the Si wafer, and was similarly formed by sputtering using the target was also set, and the average reflectance in the visible light range was measured using the optical reflectometer.

[0024]In order to evaluate a reflectance after passing through the manufacturing process as predetermined products, The reflectance after being immersed in 60 ** pure water for 30 minutes was measured as the reflectance after heat-treating the pure Ag film and Ag alloy film which formed [above-mentioned] in the temperature of 250 **, and the air of 2 hours, the reflectance at the time of neglecting 24h by the environment of the temperature of 60 **, and 90% of humidity as an environmental test, and a process examination. In order to evaluate membranous adhesion, after putting a break into the pure Ag film and Ag alloy film which heat-treated in a grid pattern at intervals of 2 mm, the tape was stuck and torn off to the membrane surface. The grid which remained on the substrate on that occasion was denoted by the area rate, and it evaluated as adhesion power. The result which more than measured is shown in Table 1.

[0025]

[Table 1]

No	組成(at%)	反射率(%)※				密着性	区 分
		成膜時	加熱処理後	環境試験後	プロセス試験後		
1	Ag	99.5	70.0	86.0	82.0	50	比較例
2	Ag- 0.10Ce- 0.50Cu	99.1	93.8	96.6	94.3	75	本発明例
3	Ag- 0.50Ce- 1.00Cu	98.5	96.6	97.4	96.8	85	本発明例
4	Ag- 2.10Ce- 0.10Cu	96.2	95.3	95.2	92.4	75	比較例
5	Ag- 0.50Nd- 0.30Cu- 0.50Au	98.7	96.2	96.7	96.8	85	本発明例
6	Ag- 0.30Nd- 1.00Au	98.6	96.2	97.4	96.5	85	本発明例
7	Ag- 1.50Nd- 1.20Pt	93.5	92.6	92.8	92.8	90	比較例
8	Ag- 0.10Gd- 0.50Au	99.1	93.7	96.6	94.2	85	本発明例
9	Ag- 0.50Gd- 0.80Au- 0.20Cu	98.1	96.1	96.9	96.4	90	本発明例
10	Ag- 1.00Gd- 0.10Au	98.6	96.8	96.6	97.1	80	本発明例
11	Ag- 2.20Gd- 1.00Pd	93.0	92.3	92.4	92.4	90	比較例
12	Ag- 0.40Gd- 0.20Au- 0.20Pt	98.7	95.6	96.6	96.1	85	本発明例
13	Ag- 0.30Gd- 0.10Pt	99.0	93.7	94.0	94.6	80	本発明例
14	Ag- 1.50Nd- 1.50Gd	95.0	94.4	94.5	85.9	65	比較例
15	Ag- 1.00Nd- 0.30Gd- 0.20Pd	98.3	97.2	97.2	97.2	85	本発明例
16	Ag- 0.20Nd- 0.20Gd- 0.60Cu	98.8	96.6	96.7	96.7	85	本発明例
17	Ag- 1.50Gd- 0.10Au- 0.20Pd	96.3	95.3	95.3	95.3	90	本発明例
18	Ag- 0.30Gd- 0.50Cu- 0.50Au	98.7	96.3	96.9	96.4	85	本発明例
19	Ag- 1.50Pd- 1.50Cu	94.0	89.0	93.0	92.0	85	比較例
20	Ag- 1.50Cu- 1.50Au	99.1	84.8	89.5	93.0	80	比較例
21	Ag- 0.50Cu	99.3	82.3	86.4	94.2	70	比較例
22	Ag- 1.50Nd	98.5	92.0	94.5	88.0	65	比較例

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[0026]Although a pure Ag film (No.1) has a very high reflectance which exceeds 99% in the time of membrane formation, it understands that the adhesion is also low while a reflectance will fall sharply, if heat-treatment and an environmental test are done. In the Ag alloy film (No.19, 20, 21) which added Pd, Cu, and Au to Ag by which the conventional proposal is made, although the reflectance at the time of membrane formation is high, the reflectance after heat-treatment falls to less than 90%, and a heat-resisting property is low. Ag understands that the reflectance after a process examination and the fall of adhesion are large in the Ag alloy film (No.14, 22) which added Nd and Gd.

[0027][the Ag alloy film containing one sort or two sorts or more of elements chosen from the group of one sort or two sorts or more of elements chosen as Ag from the group of Ce, Nd, and Gd, Cu, Au, Pd, and Pt on the other hand] Although it is lower than the Ag alloy film which added Cu, Au, and Pd to a pure Ag film or Ag about the reflectance at the time of membrane formation, it turns out that a high reflectance is maintained and adhesion is also sharply improved also after heat treatment, an environmental test, and a process examination. And the improvement effect improves by the increase in the above-mentioned amount of addition, the total quantity of each group becomes clear at more than 0.1at%, and even after doing each examination, the reflectance of not less than 93% is maintained.

[0028]However, even though there is little decline in the reflectance after each examination when the amount of these addition increases, the reflectance at the time of membrane formation falls, and the reflectance of not less than 93% becomes difficult to get (No.4, 7, 11). If the total quantity exceeds 2at%, maintenance of the reflectance of not less than 93% will become difficult, and if the total quantity exceeds 1at% also in Cu, Au, Pd, and Pt, as for Ce, Nd, and Gd, a reflectance will fall greatly.

[0029]A product is covered from the membrane formation time, and the place which is about 92%, the reflectance of a pure aluminum film can attain the reflectance beyond this, if it is an Ag alloy film of this invention. In order to obtain the higher reflectance of not less than 96% by being stabilized in the Ag alloy film of this invention, it is desirable to make into 0.3 - 0.5at% in total content of the element chosen from Cu,

Au, Pd, and Pt 0.2 - 0.5at% in total in the content of the element chosen from Ce, Nd, and Gd. Each Ag alloy film of this invention has the specific resistance of 5 or less microomegacm, and also fits the use as a low resistance metal membrane.

[0030](Embodiment 2) The Ag alloy film which produced the target and added either or the plurality, and Pd of Ce, Nd, and Gd to Ag by sputtering was formed like Embodiment 1. And at the time of membrane formation, further, the average reflectance in the visible light range after a process examination, the pure Ag film which formed similarly the reflectance of 400 nm by the side of short wavelength about the process examination back, etc. were set, and it measured. A result is shown in Table 2.

[0031]

[Table 2]

No	組成(at%)	反射率(%)※			区 分
		成膜時	プロセス試験後		
				400nm	
23	Ag	99.5	82.0	78.0	比較例
24	Ag- 0.50Ce- 0.30Pd	98.6	96.2	88.9	本発明例
25	Ag- 1.00Nd- 0.40Pd	97.0	95.7	86.5	本発明例
26	Ag- 2.00Nd- 0.20Pd	96.1	95.4	85.6	本発明例
27	Ag- 0.50Gd- 0.45Pd	98.0	95.8	87.3	本発明例
28	Ag- 0.50Gd- 0.60Pd	97.0	95.0	84.5	本発明例
29	Ag- 1.50Gd- 1.00Pd	95.5	94.7	78.0	本発明例
30	Ag- 2.00Gd- 0.50Pd	96.8	96.1	83.8	本発明例
31	Ag- 2.50Gd- 0.50Pd	94.0	93.4	81.3	比較例
32	Ag- 0.30Nd- 0.30Gd- 0.20Pd	98.3	96.1	89.1	本発明例
33	Ag- 0.20Nd- 0.20Gd- 0.40Pd	97.4	94.9	87.3	本発明例
34	Ag- 0.30Nd- 1.00Gd- 1.00Pd	94.8	93.9	81.6	本発明例
35	Ag- 1.50Pd- 1.50Cu	94.0	88.0	71.6	比較例
36	Ag- 0.50Cu	99.3	94.2	88.5	比較例
37	Ag- 1.50Nd	98.5	90.0	82.5	比較例

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[0032]After a process examination, the reflectance of a pure Ag film (No.23) is falling by the short wavelength side of a visible light range. According to this, even if it is an Ag alloy film, the reflectance by the side of the short wavelength after a process examination falls, but the decreasing rate can be made low by adding Ce, Nd, and Gd. And low resistance and the average reflectance in a visible light range itself can be highly maintained by adding Pd.

[0033]In this case, if the amount of addition of Pd increases, the reflectance by the side of short wavelength will fall, and if 0.5at% is exceeded, the reflectance of not less than 85% will become difficult to get. choosing Pd for Ce, Nd, and Gd 0.1 - 2at% in Table 2 -- 0.1 - 0.45at%, [considering it as the contained Ag alloy film] It turns out that the reflectance of not less than 85% can be maintained even if it is a short wavelength 400 nm after a process examination side, and the difference with average reflectance is acquired by stabilizing a flat reflectance optically few. In order to obtain a higher reflectance by both with an average reflectance and a reflectance of 400 nm, the content of 0.2 - 0.4at% of Pd is preferred 0.2 - 0.5at% in the sum total of Ce, Nd, and Gd.

[0034]

[Effect of the Invention]If it is this invention, it is possible to obtain the Ag alloy film for electronic parts which has improved a high reflectance and heat-resisting property, a resistance to environment, and adhesion with a substrate. Therefore, it is useful to plane display devices, such as reflective liquid crystal display in which

the low power consumption used for a Personal Digital Assistant etc. is demanded, and industrial value is high.

[Translation done.]